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Diffusion Coefficient Estimations by Thin-Channel Column Inverse Gas Chromatography : Preliminary Experiments

Mohd. Ghazali Mohd. Nawawi
Department of Chemical Engineering
Faculty of Chemical & Natural Resources Engineering
Universiti Teknologi Malaysia
Skudai, Johor, Malaysia

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ABSTRAK

Suatu turus saluran-cetek kromatografi gas telah direkabentuk dan diguna untuk menentukan pekali resapan air dan isopropanol dalam fasa polimer melalui teknik kromatografi gas songsang. Teknik ini adalah suatu teknik yang mudah, cepat dan berkesan sebagai gantian kepada kaedah erapan dan nyaherapan bagi menentukan pekali resapan bagi bahan telapan dalam berbagai filem membran polimer; teknik ini terutamanya berguna apabila masalah yang berkaitan dengan ketidakseimbangan taburan polimer menghadkan ketepatan pengukuran oleh kromatografi gas songsang. Suatu lapisan membran kitosan yang homogen telah disediakan melalui teknik tuang larutan dan digunakan sebagai fasa tetap sebagai lapisan polimer yang sekata dalam turus kromatografi gas. Penemuan awal menunjukkan bahawa pekali resapan air adalah lebih tinggi daripada pekali resapan isopropanol dan pekali resapan bertambah dengan suhu turus. Kesan saiz bahan telapan pada pekali resapan juga telah dikaji ke atas suatu siri alkohol : metanol, etanol dan isopropanol. Keputusannya mencadangkan pekali resapan dipengaruhi oleh saiz bahan telapan.

ABSTRACT

A thin-channel gas chromatography column was designed and used to measure diffusion coefficients of water and isopropanol in polymer phase via inverse gas chromatography (IGC) technique. The thin-channel column inverse gas chromatography technique proved to be a simple, fast and efficient alternative to sorption and desorption methods for measuring diffusion coefficients of permeants in thin polymer membranes films; the technique is especially useful when the problems associated with the irregularity of polymer distribution severely limit the accuracy of IGC measurement. Thin homogeneous chitosan membranes prepared by the solution casting technique were used as the stationary phase to provide a relatively uniform layer of polymer phase in the gas chromatography column. The diffusion coefficient of water was higher than that of isopropanol and diffusion coefficients of the permeants increased with column temperature. The effects of permeants size on diffusion coefficients were investigated on a series of alcohols: methanol, ethanol and isopropanol. The diffusion coefficients were inversely related to the permeants size.

Keywords: thin-channel column, gas chromatography, inverse gas chromatography, chitosan, membrane, isopropanol, water, diffusion coefficient

INTRODUCTION

Gas chromatography (GC) has become well established as an alternative for studying the interaction of polymers with volatile solutes years ago [1,2,3]. In a typical application, the polymer is used as the stationary phase in a chromatography column. The solute or probe is vaporized and injected into a carrier gas flowing through the column. As the probe is swept through the column, it can interact with the polymer via adsorption or absorption. The retention time of the probe and the shape of the elution profile (i.e. chromatographic peak) will reflect the strength and nature of the interactions that occur between the polymer and the solute and can be used to study those interactions. Such an experiment is sometimes referred to as inverse gas chromatography (IGC), to differentiate it from the more common analytical application of gas chromatography.

In general, IGC has been used primarily for the measurement of solution thermodynamic parameters. When an IGC experiment is carried out at temperatures significantly higher than the glass transition temperature of the polymeric stationary phase, the retention time will be determined by the solubility of that component in the polymer. Consequently, measurements of retention time can be used to calculate such useful parameters as Henryís law constant, the activity coefficient, and various solution model interaction parameters. In comparison with bulk equilibrium methods (gravimetric sorption/desorption) for thermodynamic measurements, IGC offers several advantages. The foremost among these is speed: a single IGC experiment can be completed in minutes; a vapor sorption experiment may require hours or days to complete.

In principle, IGC experiments can also be used to obtain information about the diffusion of the solute in the polymer phase. It has long been recognized that mass-transport limitations in the stationary phase result in significant spreading and distortion of a chromatography peak. A number of researchers have attempted to exploit this phenomenon as a means of measuring the diffusion coefficient of the solvent in the stationary phase [3-6]. In all of these studies, packed-column chromatography was used and diffusion coefficient estimates were extracted from the elution curve data using the van Deemter equation. None of these efforts has provided a convincing demonstration that the method can be used to obtain meaningful information; difficulties inherent in the use of a packed column make it nearly impossible to relate the measured elution curve to the diffusion coefficient. The major limitation is the irregular distribution of polymer within the column, which prohibits the application of realistic models for stationary phase transport processes. The van Deemter analysis assumes a uniform distribution of polymer. In any real packed column, the distribution will not be uniform and will be difficult to characterize. Pawlisch and Laurence [7,8] developed a modified mathematical model for the diffusion of solutes at infinite dilution in thin, uniform polymer films coated on glass capillary columns. Measurements were made for benzene, toluene, and ethylbenzene in polystyrene for 110° – 140 °C. The resulting values of the

diffusion coefficients were in good agreement with extrapolated values from sorption experiments [9,10].

In a pervaporation process, diffusion coefficients of permeating components in polymers in general depend strongly on the state of swelling of the polymer because of the plasticizing action of the liquid on the segmental motions of the polymer. In general, two methods have been widely used to obtain diffusion coefficients: the absorption experiment method [11,12] and the desorption experiment [13 - 15]. The two methods are based on the unsteady state process and are complicated. The experimental results are very sensitive to the accuracy of measurements. Fels and Huang [14] and Rhim and Huang [15] tried to determine the diffusion coefficients of organic components in polyethylene from desorption experiments and applied the resulting diffusion coefficients to their equations for predicting the behavior of the pervaporation process. However, the results of the comparison of the calculated data with the experimental data were not fully satisfactory. Despite the advantages and despite the widespread use of IGC, to date no attempts to utilize the use of gas chromatography to determine diffusion coefficients applicable to pervaporation process have been reported in the literature.

In this study we report the estimation of diffisuvities, methanol, ethanol, and isopropanol in the stationary column membrane made from chitosan using inverse gas chromatography method. Effects of temperature and permeant size on diffusivity have been established. A significant improvement for the diffusivity measurements by the IGC method specifically applicable to the falt-sheet pervaporation membranes have been achieved. The technique uses a specially designed column based on the concept of a thin-channel columns where a highly uniform polymer membrane is used as the stationary phase. The thin-channel column offers great improvement over the conventional packed columns where the irregularity of the coating severely limits measurement accuracy. Such a column may be used in preference to the capillary column for diffusivity studies of solutes especially in membrane research since the same membrane used in the separation processes may be employed as the stationary phase in the column.

Theory

Diffusion processes on gas chromatographic columns lead to broadening of the chromatographic peak. In traditional gas chromatography, the peak broadening is directly related to the resolving power of the columns and as such has received extensive theoretical interest [2,16]. There are two major factors that contribute to peak broadening: diffusion of the injected compound (probe) in the carrier gas and diffusion of the probe in the stationary phase. The former is characterized by the gas-phase mutual diffusion coefficient, D_g, and the latter factor is related to the liquid-phase mutual diffusion coefficient, D_L.In the case of IGC experiments, where a polymer is the stationary phase, D_L is a polymer-probe diffusion coefficient.

We will follow the standard chromatographic approach in expressing the distribution of a probe on the column by means of the height equivalent to a

theoretical plate (HETP), *H*. HETP is related to the number of theoretical plates *N* and to the physical length of the column *L* as

$$H = \frac{L}{N} \tag{1}$$

The measurements of effective diffusion coefficients were based on the well known equation developed by van Deemter et al. [17] for a gas chromatographic column:

$$H = \mathrm{A} + \frac{B}{u} + Cu \tag{2}$$

where u is the linear velocity of carrier gas and A, B and C are constants of the column, gases and operating conditions.

On packed columns, A is called the eddy diffusion term and is related to the size of the support particles and the irregularity of packing. The constant B describes the time-dependent factors; only the longitudinal diffusion of the probe, along the stream of the carrier gas, contributes significantly to B. The third term in eqn. (2) is related to peak broadening, which is due to solute/ stationary phase resistance to mass transfer within the column. The constant C is given by

$$C = \frac{8}{\pi} \frac{K}{(1 + K)^2} \frac{d^2}{D_L} \tag{3}$$

where d is the thickness of the stationary phase, D_L is the solute diffusion coefficient in the liquid phase, and K is the partition ratio given by

$$K = \frac{t_r - t_m}{t_m} \tag{4}$$

where t_r and t_m are the retention time to peak minimum of the probe molecule and a non-interacting material such as methane.

The simple version of the van Deemter equation, eqn. (3), does not consider broadening effects due to the non-instantaneous equilibration of vapor phase across the column by molecular or hydrodynamic mass transfer [18]. Trans-column diffusion in the gas phase is assumed to be fast compared with diffusion through the stationary phase. Furthermore, the assumptions used to derive the C term are unrealistic for most practical gas chromatography columns where the geometry of the column packing is very complex. Giddings [19] has developed a nonequilibrium treatment which enables calculation of peak dispersion in more complex cases by redefining the C term to take account, various dispersion factors. In the case of uniform film thickness, Giddings results are the same as that for the van Deemster C term but with the constant $8/\pi$ replaced by *2/3*. So eqn. (3) which becomes,

$$C = \frac{2}{3}\frac{K}{(1+K)^2}\frac{d^2}{D_L} \tag{5}$$

Equation (2) is only valid for describing the elution of symmetric peaks, which requires that mass-transfer resistances be small but not negligible. Equation (2) then becomes

$$H = A + \frac{B}{u} + \frac{2}{3}\frac{K}{(1+K)^2}\frac{d^2}{D_L}u \tag{6}$$

The determination of D_L involves the measurement of H at several relatively high flow rate, where the term B/u is negligible and A remains suitably small. The slope obtained in a plot of H versus u enables one to calculate D_L, since K can be directly obtained from these experiments. Thus

$$H = \frac{2}{3}\frac{K}{(1+K)^2}\frac{d^2}{D_L}u \tag{7}$$

From plate theory, it can be shown that for a column producing Gaussian-shaped peaks, H is related to the peak width or variance by [2]

$$H = L\left(\frac{\sigma_t}{t_r}\right)^2 = \frac{L}{5.54}\left(\frac{W_{1/2}}{t_r}\right)^2 \tag{8}$$

where σ_t^2 is the variance of the peak and $W_{1/2}$ is the peak width at half the peak height.

MATERIALS AND METHODS

Chitosan flakes of Flonac-N grade were obtained from Kyowa Technos Co. Ltd. Japan. Reagent grade acetic acid was purchased from Canlab, Canada. Isopropanol, ethanol and methanol obtained from Commercial Alcohols Inc. Canada were of reagent grade. Gases used for the operation of the chromatograph were supplied by Praxair, Kitchener, Ontario. A high-purity helium was used as the carrier gas, dry-grade compressed air and hydrogen were used for the flame ionization detector (FID), and methane was used as the non-interacting material.

A Hewlett Packard 5890 Series II gas chromatography equipped with both Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD) was used for the inverse gas chromatography experiments. *Fig. 1* gives a schematic of the apparatus. A hydration system is used to saturate the carrier gas with water vapour in order to swell the stationary phase to a certain extent. The flow rate of the carrier gas was controlled by a thermostated precision needle valve and was measured by soap bubble flowmeter. A 10-µl Hamilton syringe was used to inject the probes. A specially designed column is used and will be further discussed in the next section.

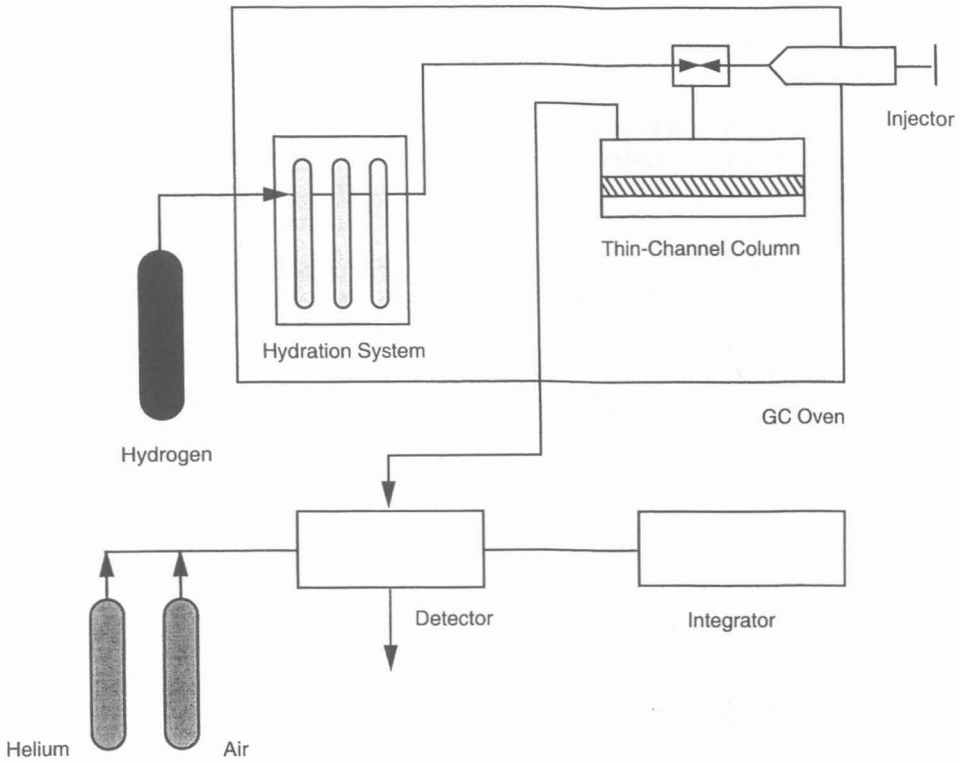

Fig 1. A schematic diagram of the apparatus used for the IGC: (1) GC oven; (2) thin-channel column; (3) hydration system; (4) detector; (5) integrator; (6) injector; (7) hydrogen; (8) helium; (9) air.

The Thin-Channel Column

The column was designed based on the concept of a spiral thin-channel system normally used for a cross-flow ultrafiltration unit. *Fig. 2* gives a schematic of the column. The column consists of two parts: the top part or the thin-channel plate and the bottom part where the stationary phase was placed. The parts were sealed together with bolts and nuts. The finished column had a thin-channel with dimensions of 3 mm in depth, 3 mm in width and 126 cm in length. The solute concentration-time profile was observed by the detector from the introduction of the solute at the injection point to its emergence at the outlet. The stationary phase which was actually a thin layer of homogeneous dense chitosan membrane was prepared according to the preparation of the pervaporation membranes [16].

Theoretically, this thin-channel gas chromatography column features a significant improvement over the more conventional packed columns. Firstly, a thin layer of dense membrane can be used as the stationary phase; in general, casting a dense membrane layer is less difficult and less time-consuming than

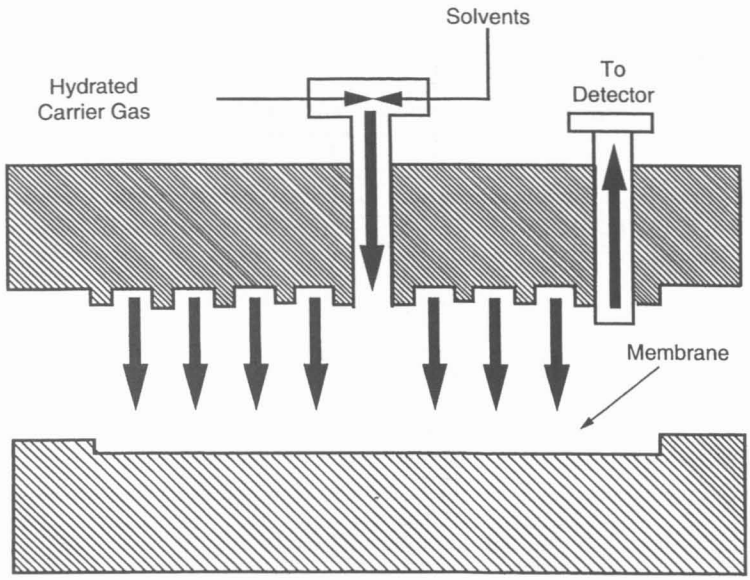

Fig 2. A schematic diagram of thin-channel GC column

preparing a packed column or coating the inner wall of a small tube. Secondly, the thickness of the stationary phase can easily be adjusted. Thirdly, the membrane can be directly cast onto the column, and most importantly, a more regular polymer distribution can be obtained.

Stationary Phase Preparation

The stationary phase consists of a thin layer of chitosan dense membrane. The membrane was prepared from a homogeneous 0.5 wt. % chitosan in acetic acid aqueous casting solution. The procedure (*Fig. 3*) involved dissolution of chitosan polymer in acetic acid to form the casting solution, casting of the polymer solution onto a glass plate to form a membrane film, treatment in sodium hydroxide solution to regenerate chitosan, washing to remove traces of alkaline solution, and drying in air to evaporate the solvent.

Experimental Procedure

The procedure for obtaining an elution curve was simple. After the GC reached stable, steady-state operations, a small amount of solvent, in liquid or vapour state, was injected into the carrier gas depending on the type of detector used, flame ionization (FID) or thermal conductivity detector (TCD). FID is only sensitive to organic substances, whereas TCD is sensitive to both organic substances and water. Vapour samples were injected into the carrier gas at the injection point (*Fig. 4*) to obtain elution curves and retention times of the probes in the swollen stationary phase and FID was used to measure the amount of solvent in the carrier gas leaving out of the column. The injection unit was

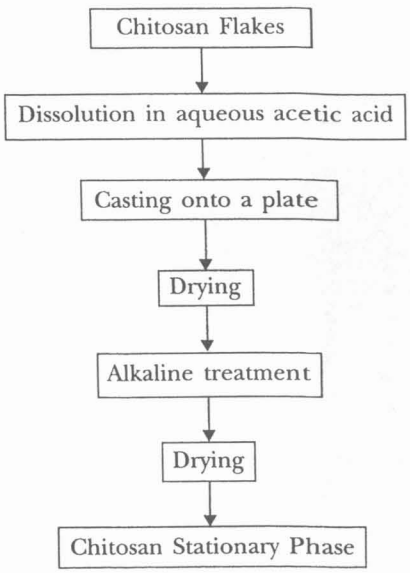

Fig. 3 Sequence of preparation of chitosan film stationary phase

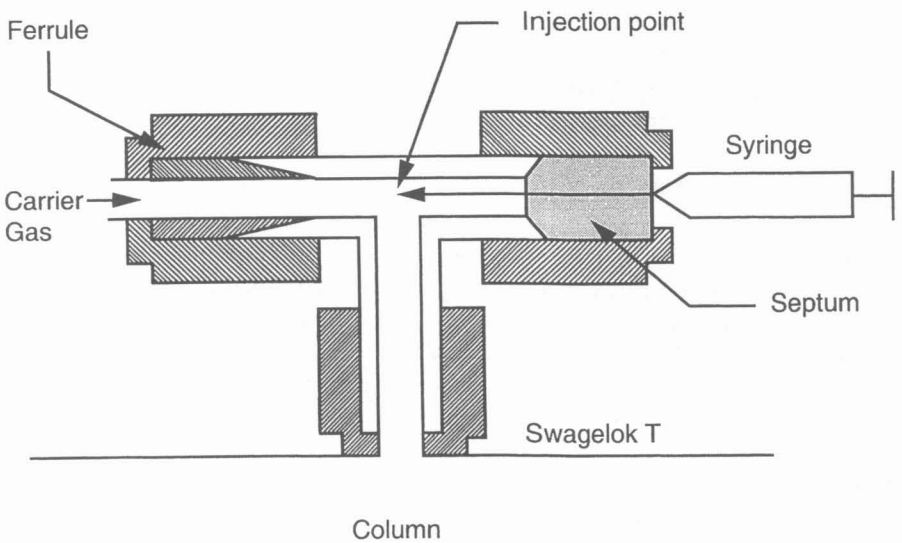

Fig 4. A schematic of the injection point of the thin-channel column

designed using a Swagelok T fitting (with an outside diameter of 3.18 mm and inside diameter of approximately 3 mm) which was directly connected to the column to minimize dead spaces or mixing. Sudden diameter changes of the fitting at the injection point that may create dead spaces or mixing was minimized. The injection unit was used in which the needle of the syringe can

be extended to the head of the column to further reduce dead spaces or mixing at the injection point. Similar design was used at the outlet point; a Swagelok fitting with an inside diameter of 3 mm allowed the column to be fastened directly to the detector.

In contrast, liquid samples were injected into the carrier gas to obtain elution curves and to determine retention times of the probes in dry stationary phase and TCD was used to measure the amount of solvent in the carrier gas leaving out the column. The liquid samples were injected through a heated injection point at 200 °C to ensure complete vaporization of the liquids. The carrier gas flow outlet flow rate was measured using a soap bubble flow meter.

The output from the gas chromatographic detector was fed to a Hewlett Packard HP 3396 Series II integrator. The experimental determination of $W_{1/2}$ and t_r was performed in triplicate for each flow rate and temperature, and an average plate height, H, was calculated. The linear portion of a graph of H vs.u was used to calculate C in the van Deemter equation (2). The value of the diffusion coefficient in the polymer membrane was calculated from C using eqn. (3). The thickness of the membrane was measured manually by using a Mitutoyo MDC Series 293 digimatic micrometer.

Measurement of Variance of Peak on Slightly Asymmetrical Peaks

When the eluted peak has a symmetrical, Gaussian profile, both the plate height, H, and the peak variance, st are easily measured. However, peaks are seldom perfectly symmetrical and the methods used to determine the necessary parameters depends very much on the degree of the asymmetry of the peaks. In this study, a simple method was used to estimate peak variance from tailed peaks obtained from the chromatogram of the solutes. This method of finding the variance involved drawing tangents on the strip-chart chromatogram through the points of inflection, i.e., steepest-slope tangents on the sides of the peak. In *Fig. 5*, the tangents are shown as intersecting the baseline at "initial" and "final" peak times, t_i and t_f. The peak variance was determined by using the equation (2)

$$\sigma_t = \frac{1}{2}\left(t_+ + t_-\right) \tag{8}$$

RESULTS AND DISCUSSION

The thin-channel column with the chitosan membrane stationary phase was used to investigate the partition coefficients of water and isopropanol. *Fig. 6* shows the effects of carrier gas velocity, u, on the partition coefficient K for both water and isopropanol at 30 °C. The small variations (near-zero slope) of K with u indicate that the partition coefficients of water and isopropanol are not dependent on the carrier gas velocity. Hence, we are justified to use the van Deemter equation to estimate diffusion coefficients of water and isopropanol in chitosan stationary phase using the thin-channel column.

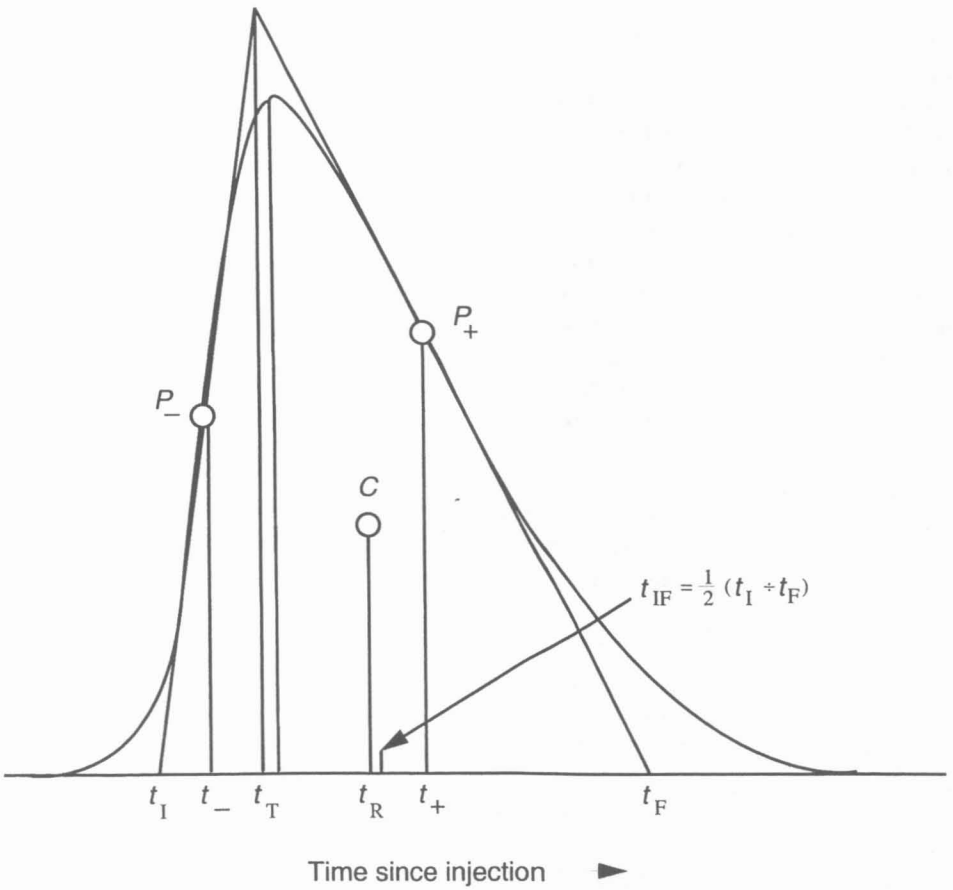

Fig 5. Times on peak concentration profile measured from mass center of injection profile, P- and P+ are the points of inflection

The thin-channel column GC technique was used to study the partition coefficients and diffusion coefficients of isopropanol, ethanol, methanol and water in the stationary phase chitosan membrane. The results of a series of experiments to measure the amount of peak spreading as a function of flow rate at room temperature are shown in *Fig.* 7. At sufficiently high flow rates, *H* increases linearly with u, with gradient C given by the simple van Deemter expression where applicable. In general, the plate heights for these experiments on polymer stationary phases are much higher than the 0.5 - 2 mm values for *H* aimed for in analytical gas chromatography [18]. High plate heights may be rationalized by considering the nature of the chitosan polymer with a glass transition temperature, T_g of about 101 °C [20]. At room temperature, chitosan contains crystalline regions which are not penetrated by the probe molecule and amorphous or rubbery regions. The rate of diffusion through this material is much slower than through the usual liquid stationary phases used in gas

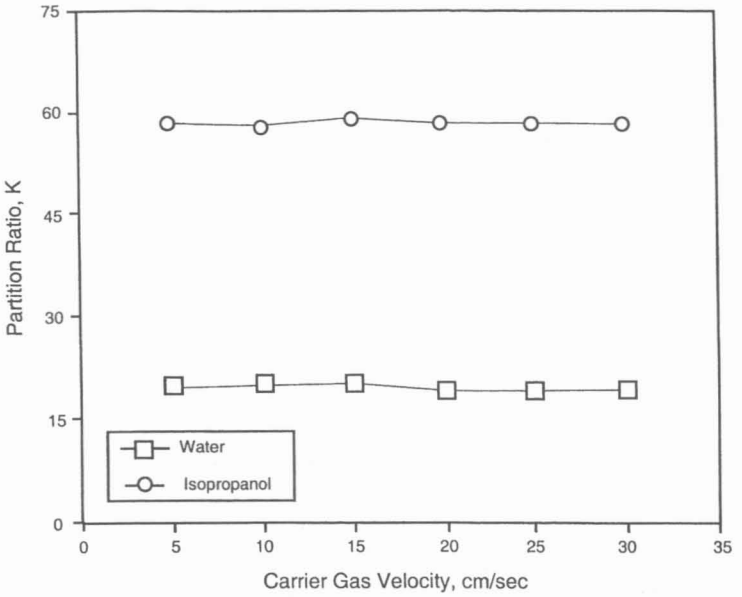

Fig 6. Partition coefficients of water and isopropanol as a function of the linear carrier gas velocity

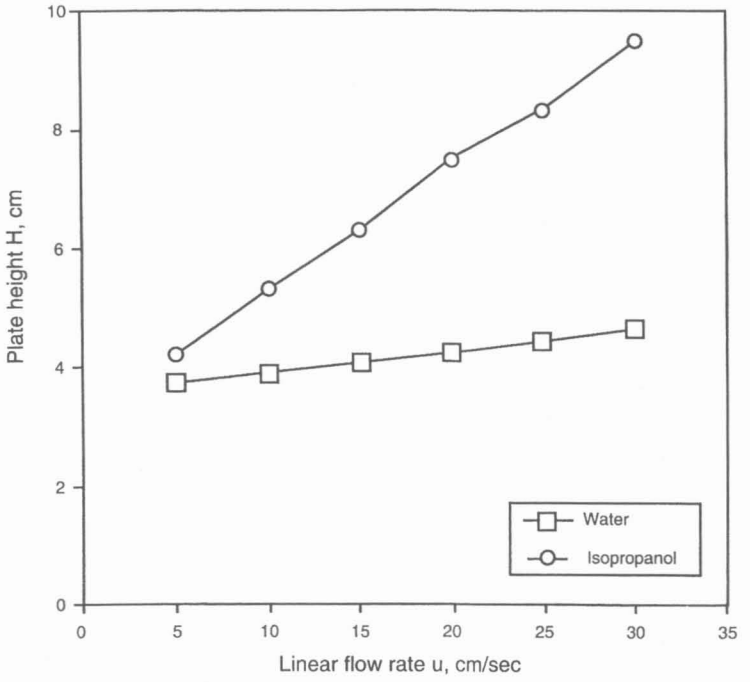

Fig 7. van Deemter curves for the thin-channel column with chitosan film stationary phase

chromatography. At temperatures below T_g, the molecular movements of the chitosan chains are limited to segmental vibrations at about a relatively fixed position. The amptitude of segmental vibration increases with increasing temperature up to T_g and at T_g; the chain segments have sufficient energy to perform rotational and translational motions or short-range diffusion motion. The plate heights of isopropanol are higher than that of water indicating that the rate of diffusion of isopropanol through the chitosan stationary phase is slower than that of water. This is not unexpected because water molecule is smaller than isopropanol molecule and generally, highly hydrophilic chitosan stationary phase exhibits stronger affinity to water relative to isopropanol. Note that this is consistent with the results obtained in the pervaporation experiments with isopropanol/water mixtures where the permeation flux of water is significantly higher than that of isopropanol for the entire range of feed composition.

The diffusion coefficients of water and isopropanol in the dry chitosan membrane at 30 °C were determined from the slope of the corresponding H versus u plots shown in *Fig. 7.* Since the slope of such a plot is equivalent to the C term in equation (2), the numerical values of the diffusion coefficients of water and isopropanol in the chitosan stationary phase could be calculated for the corresponding K values. The results are tabulated in Table 1. As expected, the diffusion coefficient of water in the chitosan membrane is larger than that of isopropanol.

Effects of Temperature

Diffusion coefficients of water and isopropanol for the chitosan stationary phase were calculated from the slopes of H vs. u. In Table 1, the diffusion coefficients of water and isopropanol are summarized along with the operating temperatures. The diffusion coefficients are of the same order of magnitude and apparently the diffusion coefficients increase with temperature from 30 to

TABLE 1
Diffusion coefficients from gas chromatography measurements

Probe	Temp. (°C)	Van Deemter C term (see 3 10^2)	K	$K/(1+K)^2$	D_L (cm^2/sec) 3 10^7
Water	30	28.5	20.7	0.044	1.03
	40	30.6	18.0	0.050	1.07
	50	30.2	16.6	0.054	1.17
	60	33.1	14.6	0.060	1.21
	70	36.5	12.3	0.070	1.28
Isopropanol	30	95.2	32.0	0.029	0.20
	40	66.6	29.7	0.032	0.32
	50	53.3	25.6	0.036	0.45
	60	48.4	21.9	0.042	0.58
	70	47.5	17.2	0.052	0.73

70 °C. An increase in temperature provides energy for a general increase in segmental motion. If the energy density is sufficient, the polymer may pass through structural transitions such as the T_g, which further affects the diffusion process. Above T_g, in the rubbery state, the segmental motion is rapid but molecular motion is still restricted by chain entanglements. As temperature increases, the degree of entanglement decreases and molecular slip increases. The effects of an increase in temperature may also be expressed in terms of the increase in free volume directly related to the bulk expansion of the polymer due to the increased segmental motions.

As shown in *Fig. 8*, the temperature dependence of diffusion coefficients, D_L over small temperature ranges can be represented by an Arrhenius type relation:

$$D_L = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{9}$$

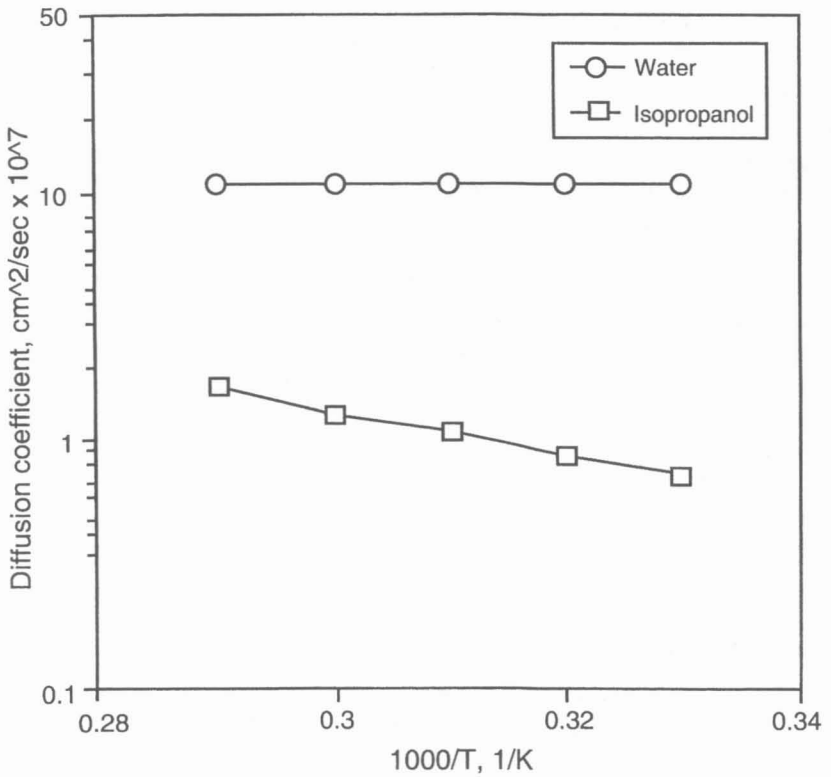

Fig 8. Arrhenius plots of diffusion coefficients for water and isopropanol in the chitosan stationary phase

where D_o is a constant, E_a the activation energy for diffusion, R the gas constant, and T_g the operating temperature. The activation energy for diffusion for water and isopropanol can be calculated from the slopes of Fig. 8 and are summarized in Table 2. The activation energy for diffusion of isopropanol is higher than that for water, which suggests that the water molecules require less energy than isopropanol does to facilitate diffusion through the stationary phase. Note that the difference in the activation energy for each probe may arise from several factors including molecular size and probe/stationary phase interaction. Interestingly, activation energy for diffusion of isopropanol through the swollen stationary phase is lower than that through the dry stationary phase. This indicates that the diffusion of isopropanol is also affected by the nature of the stationary phase; the presence of sorbed water in the water swollen stationary phase apparently decreases the energy required for the diffusion of isopropanol. Water apparently depresses the T_g of the chitosan membrane and changes the properties of the stationary phase induced by plasticisation and swelling processes. Note that plasticisation and swelling of the stationary phase caused by prolonged exposure to water saturated carrier gas are both reversible processes. The amorphous chitosan polymer exhibits a significant change from glass-like behaviour when dry to soft, rubbery-like behaviour when swollen and *vice-versa.*

Effect of Penetrant Size

An increase in the size of a penetrant in a series of chemically similar penetrants generally leads to an increase in solubility and a decrease in diffusion coefficients. The effect of penetrant size on the diffusion coefficients is illustrated in *Fig. 9* at various temperatures for a series of alcohols: methanol, ethanol and isopropanol. As can be seen, as the size of the alcohols increases from methanol to isopropanol, the corresponding diffusion coefficients decrease. The decrease in diffusion coefficients is a reflection of the need to create or utilize a critical activation volume in the polymer stationary phase proportional to that of the penetrant molecule; the size of the hole required to accommodate the molecule, the length and the size of the path the molecule must follow during its diffusion, and the free volume available to the polymer segment to exchange positions with the probe molecules.

Therefore, the diffusion coefficient shows inverse proportionality to the size of the molecule. This result agrees well with Einstein's equation [21] for

TABLE 2
Activation energy for diffusion determined by IGC technique

	Methanol (KJ/kgmol)	Ethanol (kJ/kgmol)	Isopropanol (kJ/kgmol)	Water (kJ/kgmol)
Dry Stationary Phase	0.854	0.901	1.097	0.515
Swollen Stationary Phase	0.333	0.507	0.715	–

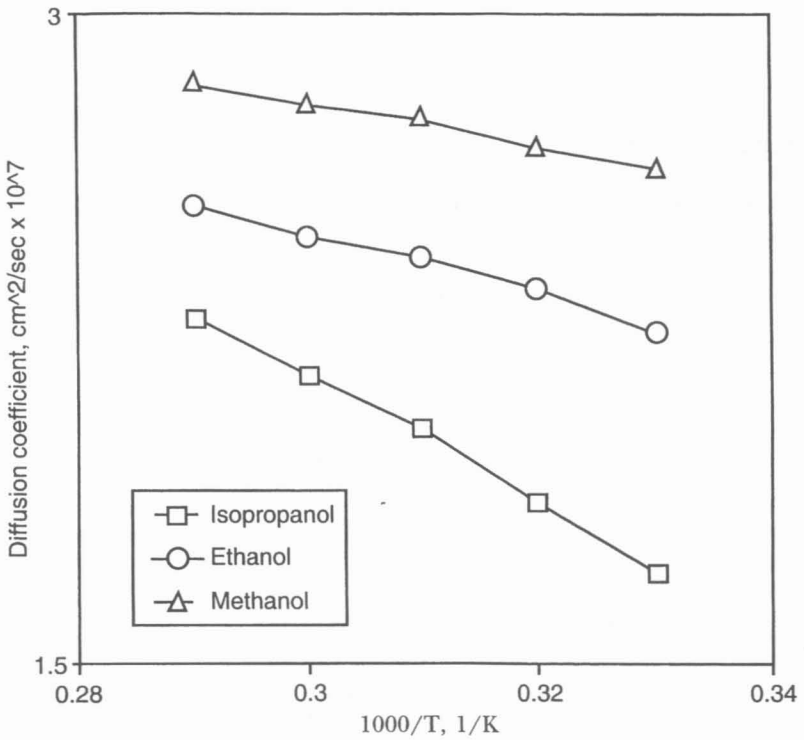

Fig 9. Arrhenius plots of diffusion coefficients of methanol, ethanol and isopropanol

the diffusion coefficient relating to the chain length of the solvent which has the form

$$D = RT/f \tag{10}$$

where f is called the friction factor and is directly proportional to the chain length. The validity of such a relationship has also been confirmed by other workers [22,23]. According to Fujita's free volume theory [24], the thermodynamic diffusion coefficient, D, is related to the free volume by the following expression:

$$D = ART\exp\left(-\frac{B}{f}\right) \tag{11}$$

where A and B are parameters that are assumed to be independent of diffusant concentration and temperature. However, A is a pre-exponential factor which depends on the properties of the diffusant and the polymer, whereas B is a constant characterizing the size of the hole needed for a diffusion jump. The fractional free volume of the pure polymer is denoted by f.

On the basis of eqn. (10), the following equation can be written for the diffusion coefficient at zero penetrant concentration, D_L:

$$D_L = ART\exp\left(-\frac{B}{f_L}\right) \tag{12}$$

where f_L is the fractional free volume of the pure polymer. Hence, increasing the diffusant size will, in general, cause an increase in B and possibly a decrease in A, which in turn decreases the diffusion coefficient.

Table 3 gives the summary of the activation energy for diffusion of methanol, ethanol and isopropanol calculated from the corresponding Arrhenius plot of diffusion coefficients. The apparent activation energy for diffusion increases proportional to the relative size of the penetrants and have the following order;

Isopropanol > ethanol > methanol

Evidently, the presence of sorbed water in the stationary phase causes a significant decrease in the activation energy. As previously discussed, swelling and plastization of the chitosan stationary phase increase the free volume available to the system to enhance the diffusion of the solvents.

Accuracy of Measurements

It is difficult to determine the accuracy of the diffusion coefficients measurements by the thin-channel column inverse gas chromatography technique. Comparison of the present results with literature data was somewhat difficult, due to unavailability of reported data on similar probe/stationary phase systems and different temperature range involved. Generally, the diffusion coefficients for polymer/probe systems lie in the range of 10^{-6} to 10^{-9} cm^2/sec [25]. The overall accuracy of the diffusion coefficients measured by the thin-channel column IGC method, as evidenced by the linearity of the Arrhenius plot of the diffusion coefficients indicated by the numerical value of the regression coefficient of determination, R^2, (see Table 3) was reasonably good.

In this work, no apparent sample-size dependent effects on the retention times were observed. Tailing and asymmetric peaks were minimal. This supports our belief that the thin-channel column "*coated*" with the chitosan membrane layer was sufficiently well-prepared, and apparatus effects were small and negligible, and that adsorption was minimized. Therefore, it was assumed that thermodynamic equilibrium was achieved in the column, and hence we were

TABLE 3
Diffusion activation energy of a series of alcohols determined by thin-channel column inverse gaschromatography technique

Chitosan Stationary Phase	Activation Energy, kJ/kgmol MeOH	EtOH	i-PrOH
Dry	0.85	0.90	1.91
Swollen	0.51	0.62	1.08

justified in using the van Deemter equation to calculate the diffusion coefficients with a high degree of accuracy. The design of the column parameters can be adjusted, within limits, to suit certain purposes and the thickness of the polymer film can be readily varied to allow for the study of a range of diffusion coefficients of components in polymeric membranes.

CONCLUSION

A spiral thin-channel column was designed and used for the study of diffusion in chitosan stationary phase based on inverse gas chromatography technique. The following conclusions can be drawn from this work:

(1) The uniquely designed column presents a reliable alternative to the conventional packed and capillary columns, for the measurements of diffusion coefficients by inverse gas chromatography technique.
(2) Inverse gas chromatography technique provides a simple, fast and objective alternative to estimate the diffusion in polymer membrane.
(3) The measured diffusion coefficients are dependent on both temperature and molecular size; the diffusion coefficients increase with an increase in temperature and decrease with an increase in molecular size of the probes.
(4) The diffusion coefficients in water swollen stationary phase are generally higher than those obtained in dry stationary phase; the sorbed water affects the diffusion of alcohols through the polymer film.

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